

10. Quality Assurance Project Plan

A Quality Assurance Project Plan (QAPP) (Worcester et al., 1995) was written at the beginning of the NMP project. The QAPP outlined objectives, procedures, and protocols for all tasks within the project, and it included information from both the Cal Poly project team and the Regional Board. The QAPP accompanied the 1993-94 annual report as a separate document.

The QAPP was reviewed in 1994 by an independent consulting firm contracted by the USEPA. Comments from the QAPP review were sent to the monitoring team. The QAPP was subsequently revised by RWQCB staff and the Cal Poly team and was returned to the USEPA for final approval. The QAPP was approved in September 1995. Copies of this document are available through the Regional Board office.

This chapter summarizes procedures and protocols not otherwise specified in the Methods sections of proceeding chapters. Results of laboratory data validation for event-based and even-interval sampling and analyses are given.

10.1 Methods

10.1.1 Watershed Maintenance

Ongoing maintenance of fences, watering systems, and farm roads was performed as needed; no protocol was established.

10.1.2 Rangeland Monitoring

Paired rangeland monitoring transects were established by matching topography and vegetation of the two paired watersheds. Transect endpoints and midpoints were marked with capped rebar and stone piles. Sampling on transects proceeded from east to west. Pace length for each sampler was determined. Biomass samples were collected at random intervals along each transect. No validation protocol was established or used for rangeland monitoring, other than trend analyses.

Paired stream reaches and transects were established based on similar streambank shapes, vegetation, channel width, and drainage area. Reach boundaries and transect endpoints were marked by rebar driven into the soil, with caps and flags at the soil surface. Stream profiles were initially measured by sag tape (Ray and Megahan, 1979). In 1994, an automatic level and stadia rod were obtained and used to measure stream profiles in subsequent years. The Pfankuch (1978) stream channel stability evaluation, modified somewhat to match local conditions, was employed to rate stream channel stability. No validation protocol was established or used for stream monitoring, other than trend analyses.

10.1.3 Sampling Protocol, Event-Based Water Quality

Sampling protocols for event-based water quality were set out in the Quality Assurance Project Plan (Worcester et al., 1996). Strict sampling protocol was established, and strict adherence was enforced throughout the project, because of the large number of samples collected and the time-critical nature of the water quality data. Sampling protocols were:

1. Inspect the sampling site for environmental conditions and for potential problems that need immediate attention.
2. Conduct preliminary sampling activities and water sample collection according to the sampling protocol.
3. Complete field sampling form. The field sampling form should be completed so that the sample bottle numbers are clearly recorded on the form. The person conducting the sampling will sign the field sampling form.
4. Complete the chain of custody form (Appendix XX).
5. Inspect sample containers for good lid closure, proper labeling, and correct numbers required for the site.
6. Return the samples to the Cal Poly Earth and Soil Sciences Department laboratory.

Water quality sampling was performed under the ultimate supervision of a Cal Poly faculty team member. Employees, consisting of part-time employees and student assistants, were trained on all sampling procedures. Instructions were printed and available to all field personnel at the gauging stations.

A number previously designated by the Project Director uniquely identified each sample. The numbers were recorded on all sampling forms, sample bottles, and lids. Numbers started with a letter (such as, W for Walters and C for Chumash). There were several sets of 24 bottles for each sampler base. Samples received at Cal Poly were kept in secured refrigerators at a temperature of 4°C ($\pm 2^\circ\text{C}$).

Formal chain of custody procedures required that possession of samples be traceable from the time of collection until completion of analytical results. A record for each sample was kept on a chain of custody form. A signature and date were required on the chain of custody record, each time custody was relinquished to another individual. A sample was considered under custody if it was in actual possession, it was in view after being in physical possession, or it was placed in a secured area after being in possession.

Samples were handled, prepared, transported, and stored with caution to minimize loss, contamination, and chemical degradation.

10.1.4 Streamflow Monitoring in the Paired Watersheds

The Parshall flume was selected, from several options of flume design, because of its ability to maintain high water velocities and keep itself clear of sediment and debris, it conforms to the natural shape of the channel, and aquatic animals can travel upstream across the flume. The design flow rate of Chumash Creek was estimated at 90 cubic feet per second (cfs). The design flow rate of Walters Creek was estimated at 100 cfs. Before the start of each rainy season, and periodically during each season, any needed

maintenance was performed at each gauging station. Routine maintenance included cleaning and testing of the flumes and monitoring equipment, calibration of potentiometers with in-stream visual gauges, and cleaning and testing of automatic samplers.

In fall 1999, the laptop PC and datalogger software were tested and updated for Y2K compliance. We purchased software upgrades from Campbell Scientific for weather station and streamflow dataloggers, since the data they collect are date- and time-dependent. After testing and updating, the PC laptop and dataloggers were field tested to verify Y2K compliance. The Sigma samplers were sent to Sigma in June 2000, for examination and troubleshooting. They were returned in September 2000.

During rainy seasons, at each sample collection and each data download, field personnel visually measured and recorded stream stage using the visual gauges mounted in each flume. These measurements served as a check of calibration of potentiometers throughout the sampling season.

10.1.5 Event-Based Water Quality Laboratory Protocol

All samples were held under refrigeration for a maximum of 24 hours after delivery to the laboratory. Undergraduate student assistants performed most laboratory analyses. Training in the procedures and laboratory safety was provided jointly by the Quality Assurance (QA) officer, laboratory coordinator (a part time employee also employed by Cal Poly), and a student lab coordinator (if such a student was available). The student lab coordinator was an undergraduate who had been employed on the project the previous year and who had demonstrated good laboratory technique, a strong sense of responsibility, and willingness to assume the duty. In addition to providing training in laboratory methods, the student lab coordinator assumed primary responsibility for arranging work schedules, seeing that work opportunities were distributed fairly, making sure samples were analyzed in a timely manner.

The Hach turbidimeter was calibrated at the beginning of each sampling season and periodically during the season. Calibration standards were prepared fresh at each calibration according to manufacturer's instructions. In addition, standards were run on the turbidimeter at the beginning of each work interval (daily or more often), to check the function of the instrument. Gelex turbidity standards were provided by the manufacturer. If values obtained were outside of the manufacturer's specified tolerances, calibration was repeated. Turbidity was measured in the lab using a Hach 2100P Turbidimeter. This instrument had an upper limit of 1000 nephelometric turbidity units (NTU). If necessary during analyses, dilutions were prepared using deionized water as the solvent. Care was taken to record the dilution factors on the data sheets, in order to correct diluted samples to true values of NTU.

Electrical conductivity was measured on unfiltered samples using a YSI Conductivity Instrument with a conductivity cell. The cell was calibrated each day using 0.01 M KCl standard as specified by the manufacturer. In the early years of the project (through 1997) temperature was recorded and temperature corrections were made to correct

readings to 25°C. Beginning in 1998, a new conductivity meter (YSI Model 3200) with automatic temperature correction was obtained by the Earth and Soil Sciences Department and loaned to the project. Conductivity was recorded in deciSiemens per meter (dS/m).

Suspended sediment concentration (filterable solids) was determined by filtering a precise aliquot of thoroughly mixed sample through pre-weighed microfilters, oven drying, and weighing to 0.1 mg. The volume of the aliquot was 100 ml for samples with low turbidity (≤ 60 NTU), 25 ml for samples with high turbidity (≥ 500 NTU), and 50 ml for other samples. In 1995, we noticed that samples of small quantity were yielding negative results - that is, weights of filters + sample were slightly lower than weights of bare filters. This occurred too often to be attributable to weighing error. We hypothesized that the filters were sorbing moisture, and beginning in 1995, filters were preweighed following oven drying.

10.1.6 Event-Based Water Quality Data Validation

Validation for laboratory data was accomplished through duplicate samples and by inspection of analytical results for trends and outliers. Decisions to disregard results as being in error were made by the QA officer or the project director (note that, beginning in 1998, these were the same person). Acceptable differences followed Regional Board protocol for even-interval sampling (Worcester et al., 1996), at the request of the Contract Manager.

Acceptable differences between first and duplicate turbidity samples were:

<u>Turbidity Range (NTU)</u>	<u>Acceptable Difference (NTU)</u>
≤ 5	± 2
≤ 25	± 5
≤ 100	± 20
≤ 500	± 50
≤ 1000	± 100
$\leq 10,000$	± 200
$\leq 100,000$	± 300

Acceptable differences between first and duplicate sediment samples were evaluated by Relative Percent Difference (RPD) (below). Acceptable RPDs were $\leq 25\%$.

$$\text{Relative Percent Difference} = \frac{(\text{First sample value} - \text{Duplicate sample value}) \times 100}{(\text{First sample value} + \text{Duplicate sample value})/2}$$

In the QAPP document (Worcester et al., 1996), it was expressed that if acceptable differences between samples and duplicates were exceeded in any analysis, that analysis was to be repeated. In practice, however, analysis of duplicate samples by the protocols above was not completed until after samples had been analyzed and discarded. The reasons for this were the pressures of the maximum allowed sample holding time, the urgent need for rapid turnover of sets of sample bottles, and the large number of samples

delivered during closely-spaced storms of high intensity. Beginning in the 1995/96 season, if the QA officer noticed differences in duplicate samples that were unduly large, she would contact laboratory personnel, individually and as a group, and review project objectives, analytical methods, and protocol.

10.2 Results

10.2.1 Rangeland and Stream Channel Monitoring

As stated above, no validation procedures were employed for collection of rangeland and stream channel monitoring, other than observation of trends. Most rangeland variables were affected by several variables (timing of cattle movement, amount and timing of rainfall, winds, humidity, soil and topographical factors), some of which were not addressed in this project. Thus, trends were not useful for assessing quality assurance.

10.2.2 Event-Based Water Quality Data Validation

Validation analyses of duplicate samples began with the 1995/96 sampling season. Most turbidity analyses were within acceptable difference. For the few duplicates that were not within the acceptable difference, trend analysis showed the first value was usually the more accurate. This value was entered into the database, and was used for water quality analyses. Our confidence in the accuracy of the “first values” is high.

Reproducibility of sediment measurements showed less reproducibility. Relative percent difference values varied between 0 percent (duplicates exactly equal, a validation of excellent laboratory technique) to, at worst, over 100 percent. Average RPD values were between 18.6 and 32 (Fig. 10.1). Of the six years analyzed, RPD for three years (1996/97, 1998/99, and 2000/01) were less than 25.

Judging from trend analysis, in most cases the first sediment value of each duplicate was the more accurate, and was entered on the database and used for analyses and discussion of water quality in response to BMP implementation.

Measurement of sediment concentration is a multistep procedure, with a multiplication factor that magnifies weighing or other errors. A small weighing error can become greatly magnified during calculations for the final answer. During training sessions, students were instructed and reminded to thoroughly mix samples before removing aliquots and to sample from the same depth in the sample container. During several laboratory observation periods, the QA officer did not observe errors in laboratory technique.

Undergraduate students were generally proud to work on this project and were anxious to do a good job. The project was regarded as prestigious, and employment on it was regarded by students as good experience and an effective resume-builder. They were aware of the goal and objectives of the project. The disadvantage of using undergraduate student assistants for data collection was the lack of continuity of trained personnel between years. Generally, students having the desired prerequisites (college chemistry and a good reference from Cal Poly faculty or staff) for employment on this project were

seniors and juniors who worked, at the most, two consecutive years on this project before graduating. Very often, students worked only one year before moving on. Lack of experience was a great, but not insurmountable, challenge to accurate data collection.

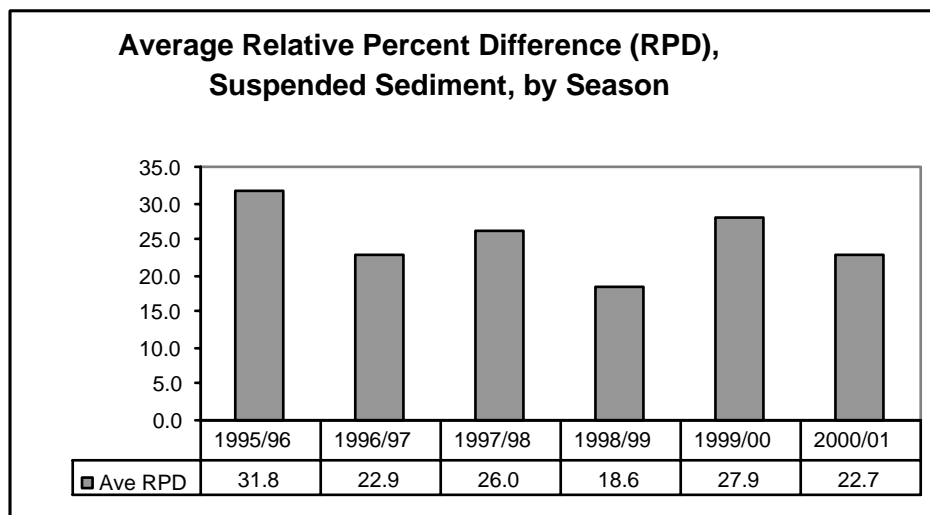


Figure 10.1. Average (by season) Relative Percent Difference between duplicate suspended sediment concentration measurements, event-based water quality.

10.3 Conclusions

Reproducibility of turbidity measurements, by the validation methods described above, was very good. Reproducibility of suspended sediment concentration was less good, because of the complicated nature of the procedure, and the magnification of small measuring errors by the multiplication step. In spite of the high RPD values for sediment, we believe sediment data are valid and meaningful. Trend analysis showed event-based suspended sediment to be congruent with turbidity and streamflow, and we used trend analysis as a tool in selecting the most likely correct measurement of each duplicate set. In fact, trend analysis itself proved to be the most useful and effective tool for quickly spotting anomalous values indicating potential laboratory errors, and quickly correcting such errors.

One exciting result from the study was the reliability of turbidity as a measure of water quality. Suspended sediment concentration correlated very well with turbidity, as shown in Chapter 3. In addition, turbidity is a much faster, less expensive, and more reliable quantity to measure, and it can be measured in the field as well as in the lab. For similar projects, Cal Poly personnel would recommend measuring turbidity with similar frequency, and measuring suspended sediment as a smaller subset, relying on a threshold value of turbidity (depending on local conditions) to determine which subset to measure suspended sediment.

The U.S. Geological Survey, an agency actively involved in hydrologic research, also found that the EPA procedure for measuring suspended sediment "...can result in

unacceptably large errors...” (Caltrans, 2001). Cal Poly personnel suggest an alternative, the SSC (suspended sediment concentration) method. This method (ASTM D 3977-97) essentially analyzes a complete water sample from a stream or other moving body of water by either of the following ways: sample evaporation, sample filtration, or wet-sieving and filtration. Which of these methods to use depends upon the characteristics of the suspended materials, mainly the amount of sands. Since the whole sample is analyzed, there is less error than trying to pipette particles out of a sample that is continually settling while the sample is being drawn.

10.4 Even-Interval Water Quality Laboratory Results

10.4.1 Calibration Procedures and Preventative Maintenance

Quality Assurance/Quality Control procedures have been carried out by following the NMP QAPP (Regional Board, 1995). Regional Board project staff have measured physical parameters, including dissolved oxygen, temperature, turbidity, conductivity, and pH using water quality instruments according to the QAPP. On May 28, 1999, a Hydrolab Surveyor 4 and Water Quality Probe were purchased to replace the Horiba and YSI meters.

10.4.2 Analytical Procedures

Bacteriological and nutrient analyses have been contracted out to the Regional Board's contract laboratory. Initially, the Regional Board's contract laboratory was Fruit Growers Laboratory. On October 10, 1995, the Regional Board contracted to another laboratory - BC Laboratories, Inc. located in Bakersfield, California. BC Laboratories' QAPP (1995) is maintained at the Regional Board office.

10.4.3 Documentation, Data Reduction and Reporting

Quality assurance verification of the NMP data began in 1999. Currently the central data base for the NMP data is an Excel Worksheet file linked to the Central Coast Ambient Monitoring Program (CCAMP). Even-interval data is kept on a shared hard drive at the Regional Board. Cal Poly provides storm-event data on zip disks, which are maintained at the Regional Board.

Some of the parameters such as ortho-phosphate as P, nitrate as NO₃, total coliform, and fecal coliform were sent to FGL Environmental (1992-1995) and BC Laboratories (1995-present). In the instance of a laboratory discrepancy, such as the absence of site tags, the lab was called directly for data verification.

Total suspended solids (tss), or filterable solids (mg/L), results are measured at the Cal Poly laboratory by Regional Board field staff. Beginning in the water year of 1996-1997, two blanks (deionized water) samples were analyzed along with samples obtained from field sites. This provides a correction factor for the sediment weight. During the first recorded water year that tss was sampled several of the holding times were exceeded, as the 7 day holding time in the protocol was identified following initiation of the analysis.

Flow (cfs), nitrate as NO₃ (mg/L), ortho-phosphate as P (mg/L), total coliform (MPN/100 ml), fecal coliform (MPN/100 ml), conductivity (ppt and uS), dissolved oxygen (ppm), water and air temperature (Celsius), and pH have been verified.

10.4.4 Data Omission

During a routine data verification to determine if the values had been entered correctly, several nitrate and ortho-phosphate values from 1998 and 1999 data points appeared suspect. The Regional Board Project Manager contacted the contract laboratory, and together they determined that the data were invalid. As a result, the sixteen dates were ultimately omitted from the dataset. To prevent future problems, the Regional Board Project Manager reviewed laboratory results routinely for abnormal patterns for the remainder of the project.

10.4.5 Data Completeness

Data verification of the past seven water years provided the opportunity to determine how accurate the data was originally entered. The continuing theme for the quality assurance program has been consistency, precision, and completeness of data entry for all parameters. Unfortunately, some electronic and hardcopy data during a portion of the post-BMP period of time were lost for several parameters. Even though, BMP evaluation continued successfully despite the missing data, and the gaps did not interfere with data analysis.

10.4.6 Data Precision

Regional Board staff evaluated even-interval data collected as duplicate samples. Since December 1993, field duplicates of bacteriological and nutrient samples have been collected during each sampling trip. Duplicate samples were taken primarily at two locations - one monitoring location on Dairy Creek (at DAU) and the other on the main stem of Chorro Creek (at CAN). Two-hundred and twenty-two (222) nutrient samples were verified with field duplicates, which is 5% of all samples taken as part of the even-interval sampling. The acceptable ranges for nitrates and phosphates according to the QAPP is a 20% Relative Percent Difference (RPD). The equation for calculating the RPD is as follows:

$$RPD = \frac{(\text{First Sample} - \text{Duplicate Sample Value}) \times 100}{(\text{First Sample} + \text{Duplicate Sample Value})/2}$$

Average RPDs for nitrate and ortho-phosphate samples were 0.57% and 3.89% respectively, which are within acceptable ranges according to the QAPP. The average values, along with other descriptive statistics are as follows:

	NO3-N	PO4-P
Count	222.00	222.00
Average	-0.17%	3.89%
Median	0.00%	0.00%
Min	-191.92%	-197.52%
Max	194.74%	175.59%

Regional Board Project Staff evaluated duplicate fecal coliform samples to determine whether or not they were within an acceptable range. The acceptable range for total and fecal coliform can be found in Standard Methods for the Examination of Water and Wastewater (Eaton, et. al., 1995). Standard Methods outlines the methods suitable to analyze water quality and water pollution and the 95% confidence limits for various combinations of positive results. Total and fecal coliform MPN index values were compared to the 95% confidence limits. 25-tube test was used, and Standard Methods specifies methods for a 5-tube test. For coliform levels that exceeded those found in Standard Methods, Regional Board staff extrapolated to obtain the greater values by multiplying by factors of ten, as the test relies on dilutions of ten. The most conservative confidence interval was used.

Two hundred and sixty-nine (247) samples were verified with duplicates. The average percent outside the confidence limit was 25.9%. The results for each site where duplicates were taken are as follows:

Site	# outside confidence			
	interval	total	percent	
CAN		29	117	24.8%
CVC		2	16	12.5%
DAM		0	3	0.0%
DAU		33	111	29.7%
Totals		64	247	25.9%

Regional Board Project Staff had initially taken duplicated turbidity samples and analyzed them using two different meters at the Regional Board and at Cal Poly laboratories. Results of the evaluation were not valid, however, because duplicate sample holding times were exceeded.

10.4.7 Performance and System Audits

The Regional Board Project Manager reviewed calibration procedures, accompanied field samplers to National Monitoring Program sites, and verified data entry and management throughout the water year. Data management concerns have been identified in the previous sections.

10.4.8 Corrective Action

Field duplicate quality assurance results for nutrient and bacteriological samples were obtained and compared to determine data precision as discussed above. These data could be voided from statistical analysis, however this is not recommended because it would remove variability and reduce sample size.